Hafnium dioxide etch-stop layer for phase-shifting masks

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Phase-shift masks were prepared using sputter deposited films for the phase-shift layer and etch stop layer on fused quartz silica substrates. It has been found that the combination of SiO_2 for the phase-shift layer and HfO_2 for the etch-stop layer offers a unique combination of properties advantageous for the preparation of phase-shift masks. The optical transmission properties of HfO_2 layers with or without a SiO_2 phase-shifting layer on quartz substrates are presented.

The use of the phase shift approach to increase the resolution of lithography has been reported.[1–4] Several methods have been reported for obtaining the 180° optical phase-shift pattern. Etching into the surface of the quartz plate has a number of advantages but requires great care in etching uniformly to the correct depth. Spin-on-glass layers have also been reported. These require special thermal processing to achieve the desired properties. We have investigated the use of sputtered films of SiO_2. In order to etch the phase-shift layer without etching the quartz substrates, an etch-stop layer is necessary. Al_2O_3 (Ref. 5) has been recommended as an etch-stop layer because it has good optical transmission at *i* line and in the deep UV, and it also has good etch selectively for the SiO_2 phase-shift layer. We have found that it is difficult to produce Al_2O_3 films that are resistant to typical chemical cleaning process (e.g., 4:1 H_2SO_4: H_2O_2 at 90 °C). Also the films are typically highly stressed, which is very undesirable for the phase-shift mask (PSM) application due to the high level of flatness required of the substrates. Although methods can be found to produce high-quality films,[6] alternative materials were sought for this application. We have reviewed the literature and found that HfO_2 films have good UV transmission properties and are difficult to etch. Since the other properties of HfO_2 films are not well known, it is of interest to study them and to determine whether HfO_2 films are good etch-stop layers for PSMs.

We then discovered that HfO_2 films not only have good optical transmission at *i* line and deep UV, good etch selectivity with the SiO_2 phase-shifting layer, low film stress on quartz substrates, but are also not attacked by the chemical cleaning solution at 90 °C. The HfO_2 films were deposited by a rf sputtering process. The sputtering system was evacuated to less than 10^{-7} Torr by a turbomolecular pump prior to the introduction of the argon–oxygen gas mixture. 5 in.^{2} fused silica plates were used as substrates and were mounted on a water-cooled 8 in. diam plate. During the deposition input power was between 200 and 400 W. Argon–oxygen gas mixture was used, and the total pressure was 5 mTorr. The oxygen content in the sputtering gas was ~10%; oxygen contents as high as 40% have been used with no significant effects on deposited films. After deposition, thicknesses were determined by a Tencor Alpha-step Profilometer. Films were grown with thicknesses varying from ~50 to 105 nm. For some of the samples, SiO_2 phase-shifting layers were deposited on top of some HfO_2 films for the study of their optical properties. Optical transmission was measured using a Varian DMS-

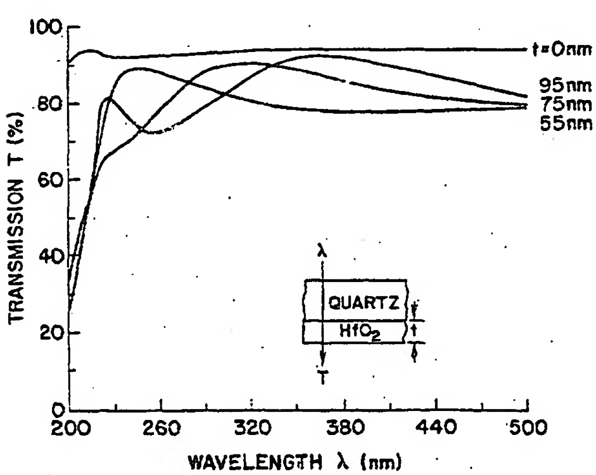

FIG. 1. Optical transmission of HfO_2 films with different thickness on fused quartz substrates.

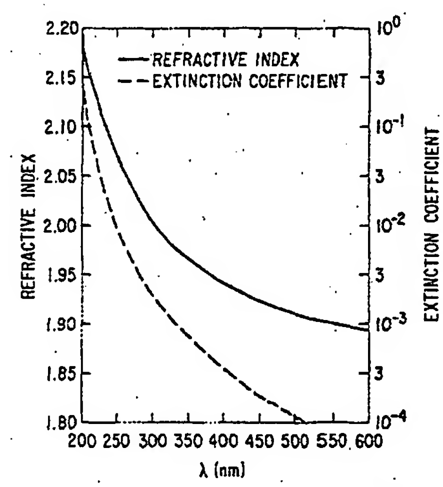

FIG. 2. Refractive index of HfO_2 on quartz substrates between 200 and 600 nm.

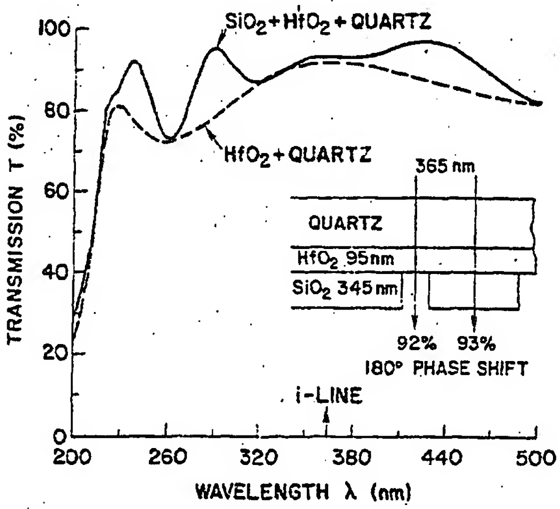

FIG. 3. Optical transmission spectra of a PSM designed for an *i*-line (365 nm) stepper.

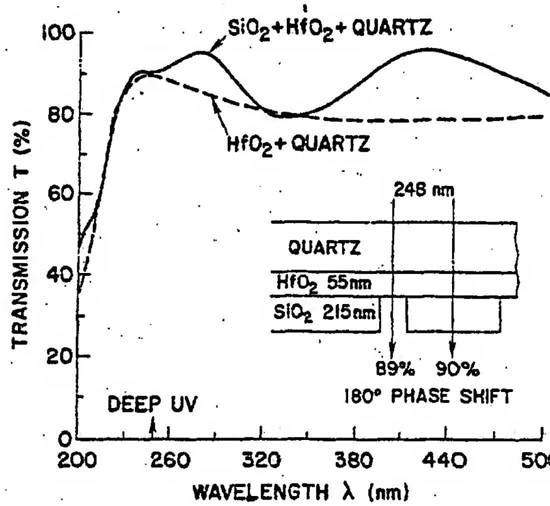

FIG. 4. Optical transmission spectra of a PSM designed for a deep-UV (248 nm) stepper.

200 UV visible spectrophotometer. The film stress was measured by observing interference fringes between the surface of the silica plate and an optical flat plate before and after film deposition.

The stress of HfO_2 films is sufficiently low that no more than two fringes between the coated substrates and the optical flat plate was observed. The HfO_2 film etch rate was evaluated using reactive ion etching (RIE) employed for patterning the SiO_2 layer. We tested the etch rate on a Plasma-Therm RIE system using CHF_3 gas at 100 W power and 50–100 mTorr pressure. A series of runs was carried out to determine the optimum SiO_2 etching conditions. It was found that the ratio of etch rate for HfO_2 to SiO_2 is better than 1 to 16. These results of etch studies will be reported in detail in another article.[7]

The transparency of HfO_2 films deposited on quartz substrates was measured from 200 to 500 nm as a function of film thickness, and the results are shown in Fig. 1. As shown in Fig. 1, for *i*-line application, a film with a thickness of ~95 nm had an optical transmission of ~92% at 365 nm. With decreasing thickness, the peak shifts to lower wavelength. The optical transmission is ~89% at 248 nm at a film thickness of ~55 nm.

The refractive index and extinction coefficient of films on quartz between 200 and 600 nm were calculated using a computer fit to the optical transmission curves for the given thickness of the films. The results are shown in Fig. 2.

Figure 3 shows the measured optical transmission spectra of a PSM designed for an *i*-line stepper. The thickness of the etch-stop layer was ~95 nm and that of the phase-shifting layer was ~345 nm. A small transparency difference of ~1% was observed. Figure 4 shows the measured optical transmission spectra of a PSM designed for deep UV at 248 nm. In this case, the thickness of the etch-stop layer is ~55 nm and the phase-shifting layer ~215 nm. Also, there is a small difference between the transmission with and without the SiO_2 layer at 248 nm. We have made a series of PSMs using these materials with etched patterns on 5 and 6 in.[2] quartz substrates. Details of design and fabrication of these masks will be published later.[7]

In summary, we have found that HfO_2 films can be used as etch-stop layers for PSMs. The films have good optical transmission at 365 and 248 nm and high etching selectively compared to SiO_2 film. This material also is chemically stable and not attacked by chemical cleaning solutions. In general, the sputtered HfO_2 films have been found to be very reproducible and are easily prepared in the chemically resistant, low stress condition.

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